

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 378 248
A2

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **90103567.5**(51) Int. Cl.⁵: **C08F 10/04, C08F 10/14**(22) Date of filing: **12.02.86**

This application was filed on 23-02-1990 as a
divisional application to the application
mentioned under INID code 60.

(30) Priority: **13.02.85 DE 3504809**(43) Date of publication of application:
18.07.90 Bulletin 90/29(60) Publication number of the earlier application in
accordance with Art.76 EPC: **0 194 456**(84) Designated Contracting States:
AT BE CH DE FR GB IT LI LU NL(71) Applicant: **Studiengesellschaft Kohle mbH**
Kaiser-Wilhelm-Platz 1
D-4330 Mülheim/Ruhr(DE)(72) Inventor: **Fink, Gerhard, Dr.**
Lembkestrasse 5
D-4330 Mülheim/Ruhr(DE)
Inventor: **Möhring, Volker**
Lembkestrasse 5
D-4330 Mülheim/Ruhr(DE)(74) Representative: **von Kreisler, Alek,**
Dipl.-Chem. et al
Patentanwälte Von Kreisler-Selting-Werner
Deichmannhaus am Hauptbahnhof
D-5000 Köln 1(DE)(54) **Process for preparing alpha-olefin polymers and oligomers.**

(57) The invention relates to polymers and oligomers characterized in that they have been prepared from α -olefin monomers or mixtures thereof and the distances between the methyl branching points are controllable by the selection of the α -olefins and to a process for preparing said novel polymers and oligomers.

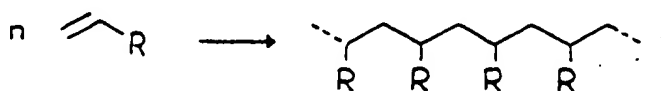
Best Available Copy

EP 0 378 248 A2

PROCESS FOR PREPARING α -OLEFIN POLYMERS AND OLIGOMERS

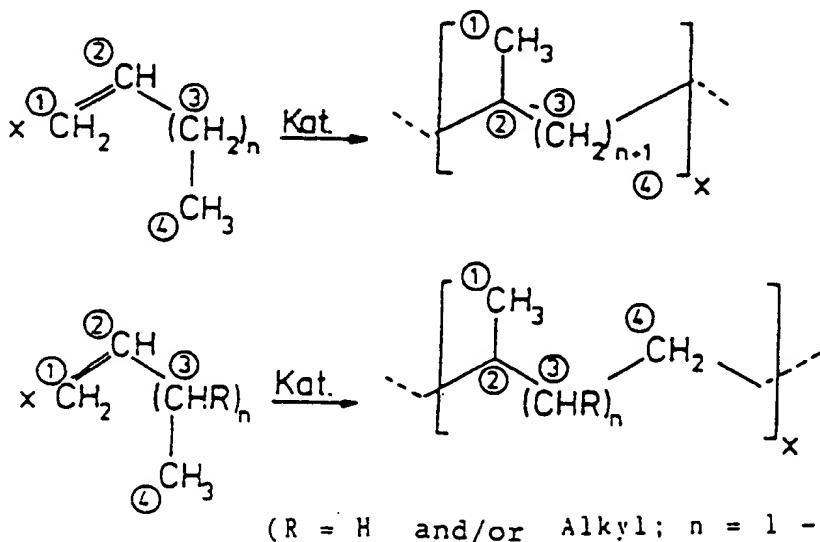
The present invention relates to a process for preparing polymers and oligomers of α -olefins having sites of methyl branching at defined distances which are adjustable due to the selection of the α -olefin.

The polymerization and oligomerization of α -olefins which is known to be achievable by use of a variety of catalysts leads to the formation of products containing 1,2-linkages of the α -olefins. The olefinic carbon atoms form the main chain in the product, while the residue R appears as the side-chain:

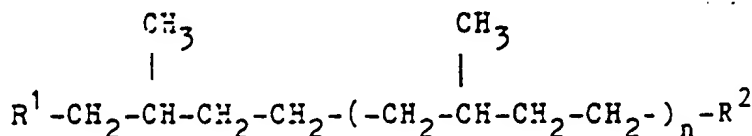


Now it has surprisingly been found that it is possible to link α -olefins with high product yields in a way different from that described above and thereby to produce structural units which so far have been not known for α -olefin polymers.

According to the present invention, the part $-\text{CH}_2-\text{R}$ of an α -olefin $\text{CH}_2=\text{CH}-\text{CH}_2\text{R}$ has been incorporated in the main chain whereby methyl side-chains are formed at definite distances depending on the employed species of α -olefin. Thus, when linear α -olefins are employed, products are formed which correspond to a 2, ω -linkage.



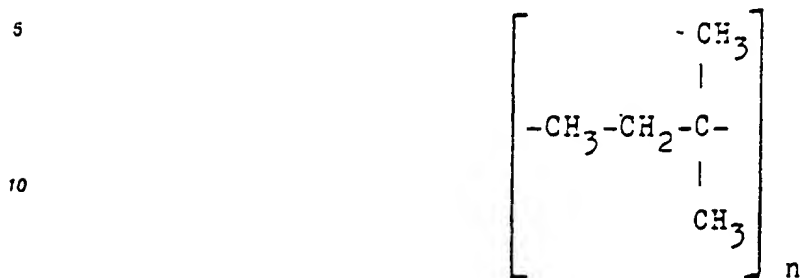
Polymers having such a structure have not been known so far. In the German Offenlegungsschrift (DE-OS) 26 23 718 S. Yasui et al. obtain, by hydrogenation of polyisoprene oils, a mixture which allegedly contains 70% of a 1,4-polymer having the structure



Nothing has been mentioned on either the residues nor on any evidence of the above configuration.

In the DE-OS 21 01 069 dal'Asta et al. describe elastomeric hydrocarbons which *inter alia* are obtained by hydrogenation of poly-2,3-dimethylbutadiene. Here, as in similar cases of the DE-OS, a mixture of cyclic

oligomers and linear head-tail, head-head and tail-tail oligomers is obtained. The cationic polymerization of 3-methylbutene-1 with AlCl_3 results in the formation of polymers having a probable structure represented by the formula



[I.P. Kennedy et al., Makromolekulare Chemie 53 (1962), page 28]. All of the mentioned processes lead to mixtures comprising polymers part of which has not been identified, some of them elastomers, however not to uniform oligomers having the structure shown above.

According to the present invention the distances between the branching points of the methyl groups can be defined as desired by selecting a pertinent α -olefin. Thus, upon use of a linear α -olefin having n CH_2 groups there are obtained distances amounting to $(n + 1)$ CH_2 groups.

The structures of the products obtained in the α -olefin polymerization according to the present invention can be proven of by means of ^{13}C NMR investigations. The chemical shifts of the carbon atoms were calculated for the respective structures to be expected in accordance with the increment rules established by L.P. Lindemann and J.Q. Adams [Anal. Chem. 43, 1245 (1971)]. Spectra simulated by using these data together with the corresponding intensities were compared to the Spectra No. 1 to 7 as experimentally obtained.

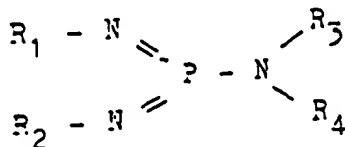
Spectrum No. 1 shows the recorded ^{13}C NMR spectrum of the butene-1 polymer. All of the signals obtained in simulation using $z = 2$ (z = number of the CH_2 groups between the methyl branching points of the polymer) are found in the experimental spectrum. The conformity becomes even more distinctly evident with increasing chain length of the starting α -olefin.

Due to their defined structures which may be subject to controlled variations within a wide range, the products offer themselves as model substances for physical investigations. By introducing functional groups at the sites of the methyl side chains of the product there can be prepared subsequent products bearing regularly distributed functions. As the functional groups are spaced apart at precisely defined variable distances along the main chain, there is a possibility of, e.g., producing novel regular graft polymers. Furthermore, upon a successive use of different α -olefins, block copolymers will become accessible which have different branching distances. The regular structure of the polymers causes a high thermal lubricant stability to be achieved.

The described new α -olefin polymers are obtainable in high yield by using a catalyst system which consists of the following components:

a) a $\text{Ni}(\text{O})$ compound NiL_x , wherein the ligand(s) L may be hydrocarbon compounds and/or hydrogen and

b) an aminobis(imino)phosphorane represented by the formula



wherein R_1 to R_4 may be same or different and represent n - or iso-alkyl groups, aryl groups and/or trialkylsilyl groups.

The $\text{Ni}(\text{O})$ compound preferably comprises unsaturated hydrocarbon ligands such as, e.g., ethylene, cyclooctadiene-1,5, cyclododecatriene-1,5,9, cyclooctatetraene etc.. They may also be produced by reduction of a suitable higher-valent nickel compound in the reaction solution.

The second catalyst component preferably consists of a trimethylsilyl-substituted phosphorane



5

19

30

30

39

EXAMPLE 1

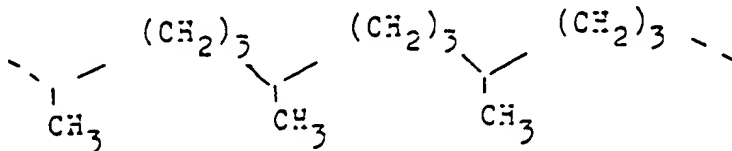
40



54

EXAMPLE 2

In a glass vessel pre-conditioned by heating under vacuum and filled with argon 0.34 g of (cyclododecatriene-1,5,9)nickel and 0.56 g of bis(trimethylsilyl)amino-bis(trimethylsilylimino)phosphorane were dissolved in 18 ml of pentene-1, and the solution was stirred at 0 °C for 24 hours. After a working-up procedure as described in Example 1 there were obtained 8.4 g (73%) of poly-2,5-(pentene-1) ($M_n = 100$):

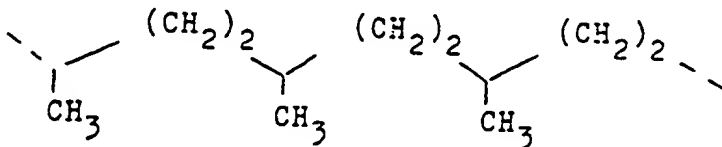


^{13}C NMR Spectrum No. 2.

(This structure conforms to a strictly alternating ethene/propene copolymer!)

EXAMPLE 3

A 100 ml steel autoclave which had been evacuated and filled with argon was charged with a solution of 0.69 g of bis(cyclooctadiene-1,5)nickel and 0.92 g of bis(trimethylsilyl)amino-bis(trimethylsilylimino)-phosphorane in 30 ml of dry toluene. Upon addition of 18 g of liquefied butene-1 the mixture was stirred at room temperature for 3 hours. After a working-up procedure as described in Example 1 there were obtained 11.6 g (66%) of poly-2,4-(butene-1) ($M_n = 900$):



^{13}C NMR Spectrum No. 1.

EXAMPLE 4

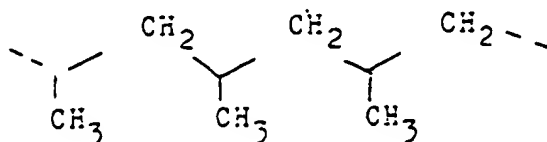
In a glass vessel pre-conditioned by heating under vacuum and filled with argon 0.17 g (0.62 mmol) of bis(cyclooctadiene-1,5)nickel and 0.92 g (2.5 mmol) of bis(trimethylsilyl)amino-bis(trimethylsilylimino)-phosphorane were dissolved in 30 ml of pentene-1, and the solution was stirred at 0 °C for 24 hours. After a working-up procedure as described in Example 1 there were obtained 17.4 g (91%) of poly-2,5-(pentene-1) ($M_n = 1300$). The structure was in accordance with the product of Example 2. ^{13}C NMR Spectrum No. 2.

EXAMPLE 5

In a glass vessel pre-conditioned by heating under vacuum and filled with argon 0.34 g (1.24 mmol) of bis(cyclooctadiene-1,5)nickel and 0.46 g (1.25 mmol) of bis(trimethylsilyl)amino-bis(trimethylsilylimino)-phosphorane were dissolved in 20 ml of decene-1, and the solution was stirred at 0 °C for 3 hours. Then to the gel-like mass there were added 20 ml of hexene-1, and the mixture was stirred at 0 °C for another 4 hours. After a working-up procedure as described in Example 1 there were obtained 24.0 g (85% of the total amount) of a decene-1/hexene-1 block copolymer which had a methyl branching point characteristic corresponding to the molar ratio of the α -olefin reactants ($M_n = 1900$).

EXAMPLE 6

In a glass vessel pre-conditioned by heating under vacuum and filled with argon 0.34 g (1.24 mmol) of bis(cyclooctadiene-1,5)nickel and 0.46 g (1.25 mmol) of bis(trimethylsilyl)amino-bis(trimethylsilylimino)-phosphorane were dissolved in 20 ml of dry toluene. Upon addition of 10 ml of 4-methylpentene-1 the solution was stirred at room temperature for 3 hours. After a working-up procedure as described in Example 1 there were obtained 3.7 g (56%) of poly-2,5-(4-methylpentene-1) ($M_n = 800$):

EXAMPLE 7

In a glass vessel pre-conditioned by heating under vacuum and filled with argon 0.34 g of bis(cyclooctadiene-1,5)nickel and 0.46 g of bis(trimethylsilyl)amino-bis(trimethylsilylimino)phosphorane were dissolved in 20 ml of dry toluene, and upon addition of 7.0 g of eicosene-1 the solution was stirred at room temperature for 14 days. After a working-up procedure as described in Example 1 there were obtained 2.4 g (34%) of poly-2,20-(eicosene-1) ($M_n = 1\ 200$).

EXAMPLES 8 to 11

Heptene-1, octene-1, nonene-1 and decene-1 were reacted using the procedures of the Examples as indicated in the following Table which also shows the obtained yields and M_n values.

Table

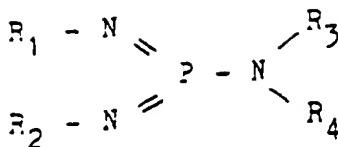
α -Olefin Polymerization:				
α -olefin	according to Example	temperature (°C)	yield (%)	M_n
Heptene-1	4	0	66	1 200
Octene-1	2	0	67	1 300
Nonene-1	4	25	32	1 000
Decene-1	1	25	27	1 300

The ¹³C NMR Spectra Nos. 4 to 7 were measured using respective product samples.

A process for preparing novel polymers and oligomers, characterized in that α -olefins having more than 3 carbon atoms are polymerized in solvents or in the liquid monomer at a temperature between -78°C and 80°C in the presence of a catalyst system which consists of

a) a Ni(O) compound NiL_x , wherein the ligand L may be a hydrocarbon compound and/or hydrogen and

b) an aminobis(imino)phosphorane represented by the formula



wherein R_1 to R_4 may be same or different and represent *n*- and iso-alkyl groups, aryl groups and/or trialkylsilyl groups.

The process as indicated above, characterized in that it is preferred to be carried out in the presence of a catalyst system consisting of

a) a Ni(O) compound NiL_x , wherein the ligand(s) L may be selected from the group consisting of hydrocarbons having one or several double bonds such as, e.g., ethylene, cyclooctadiene-1,5, cyclododecatriene-1,5,9, cyclooctatetraene etc. and

b) the aminobis(imino)phosphorane wherein $R_1 = R_2 = R_3 = R_4 = Si(CH_3)_3$

The process as indicated above, characterized in that the Ni(O) compound has been produced "in situ" in the reaction solution by reduction of a suitable higher-valent Ni compound.

The process as indicated above, characterized in that as solvents, if employed, aromatic and/or olefinic hydrocarbons are used.

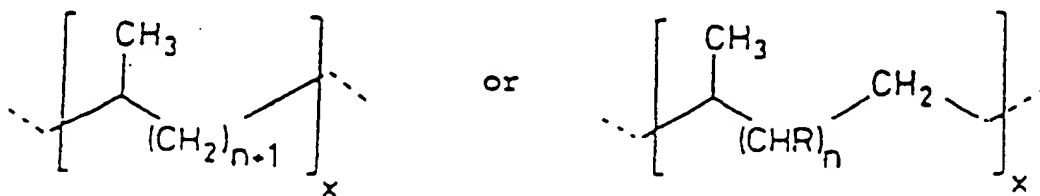
The process as indicated above, characterized in that

- the concentration of the Ni(O) compound preferably is from 10^{-3} to 10^{-1} mol/l,
- the molar ratio of the Ni(O) compound to the aminobis(imino)phosphorane is from 1:1 to 1:100, and preferably from 1:1 to 1:10, and
- the reaction temperature preferably is from $-20^\circ C$ to $+30^\circ C$.

The process as indicated above, characterized in that the employed α -olefin is linear or branched, unsubstituted or substituted with (cyclic) alkyl groups, and preferably has a number of carbon atoms of between 4 and 20.

Claims

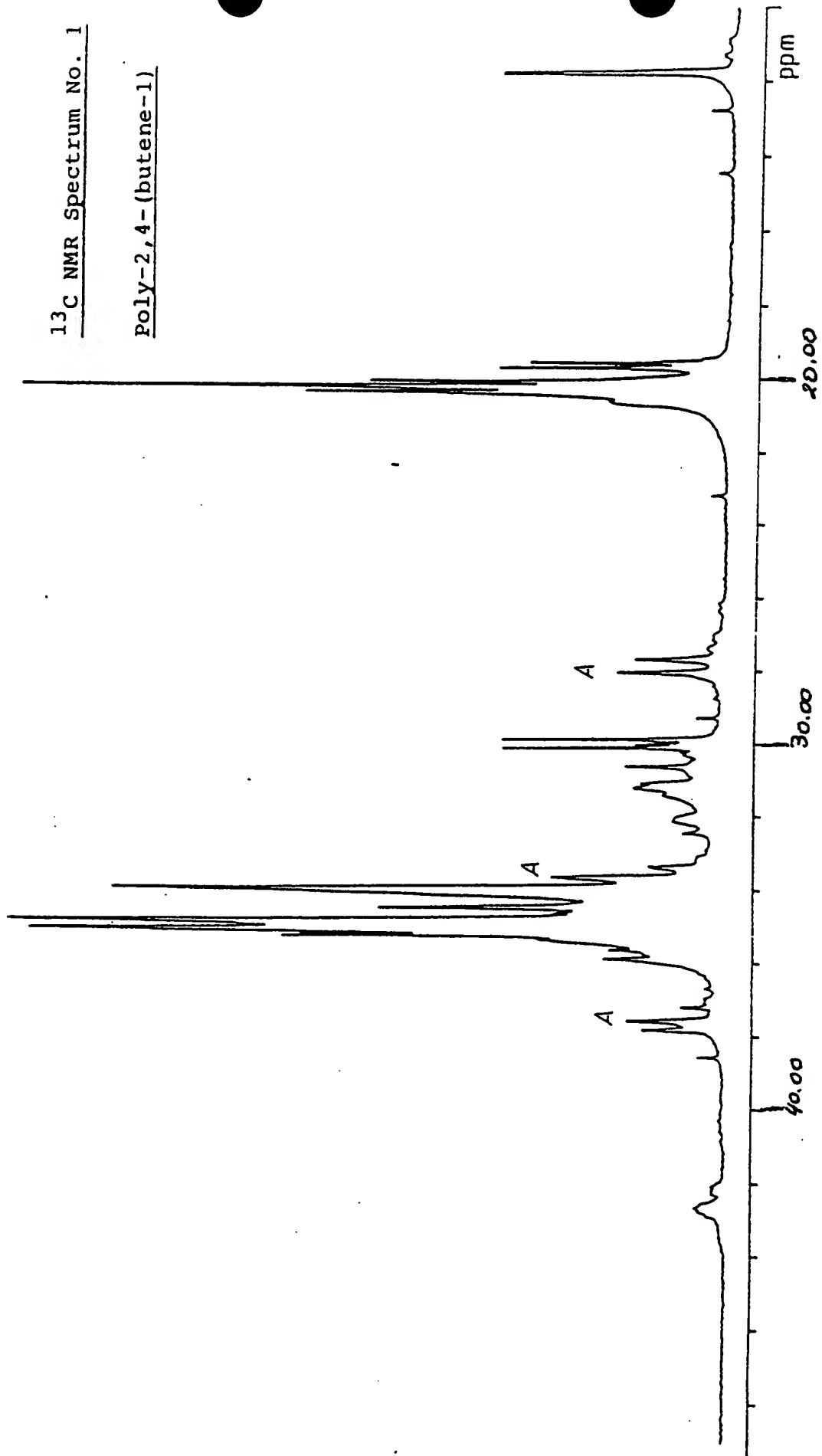
1. Polymers and oligomers, characterized in that they have been prepared from α -olefin monomers having more than 3 carbon atoms or mixtures thereof and the distances of the methyl branching points are controllable by the selection of the α -olefins and the polymers are defined by having the following structures



wherein $R = H$ and/or Alkyl; $n = 1 - 17$.

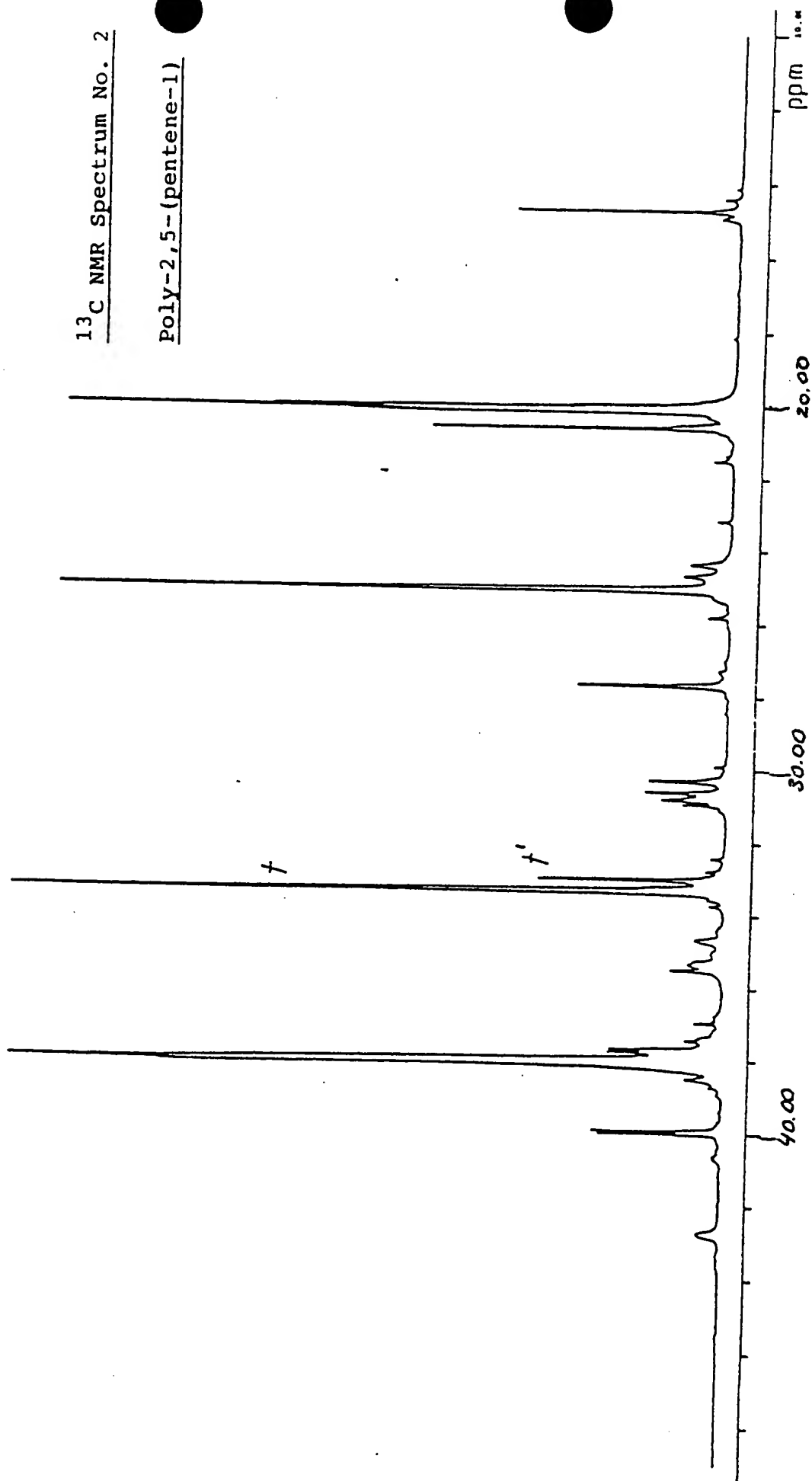
^{13}C NMR Spectrum No. 1

Poly-2,4-(butene-1)



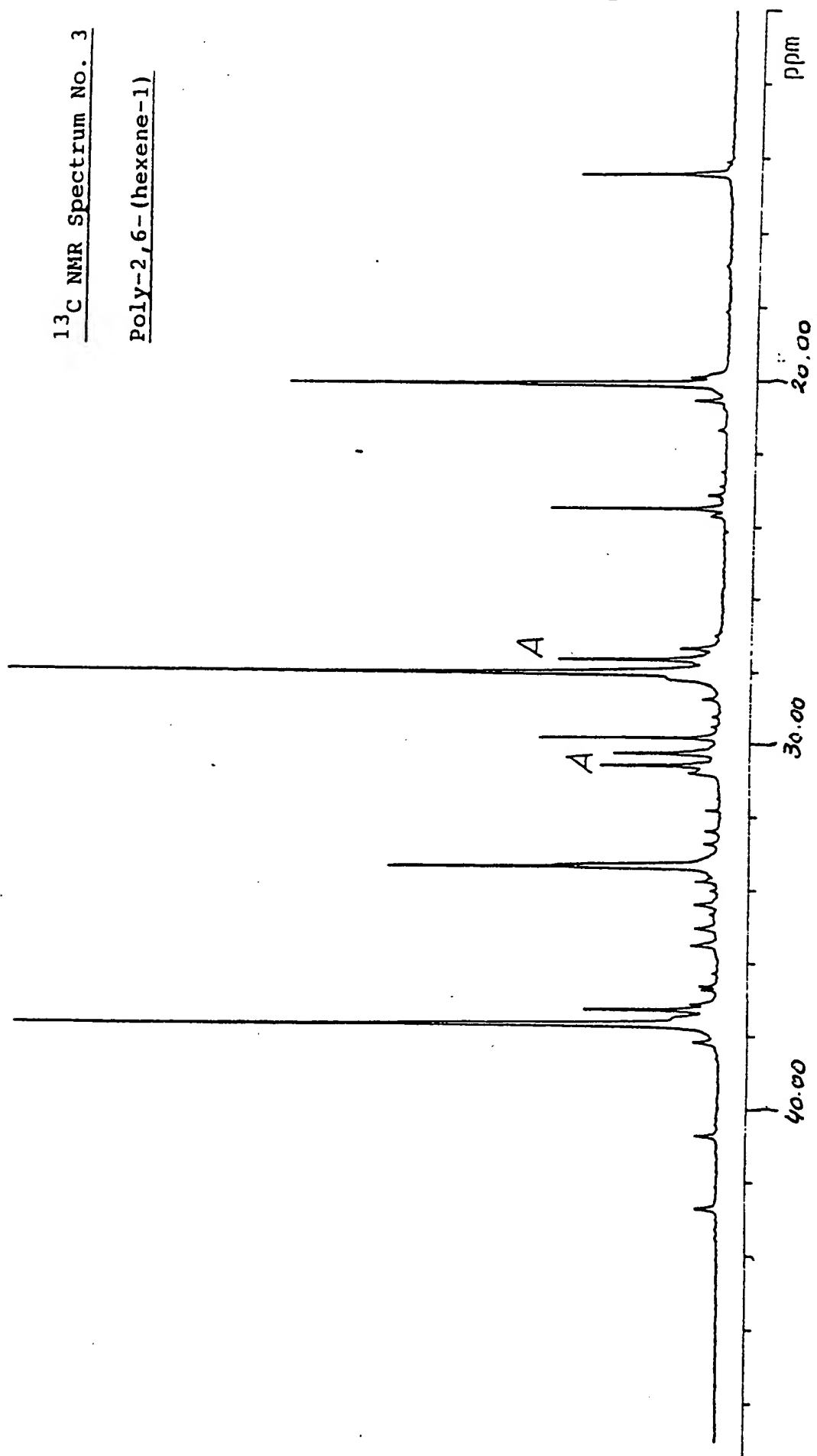
^{13}C NMR Spectrum No. 2

Poly-2,5-(pentene-1)



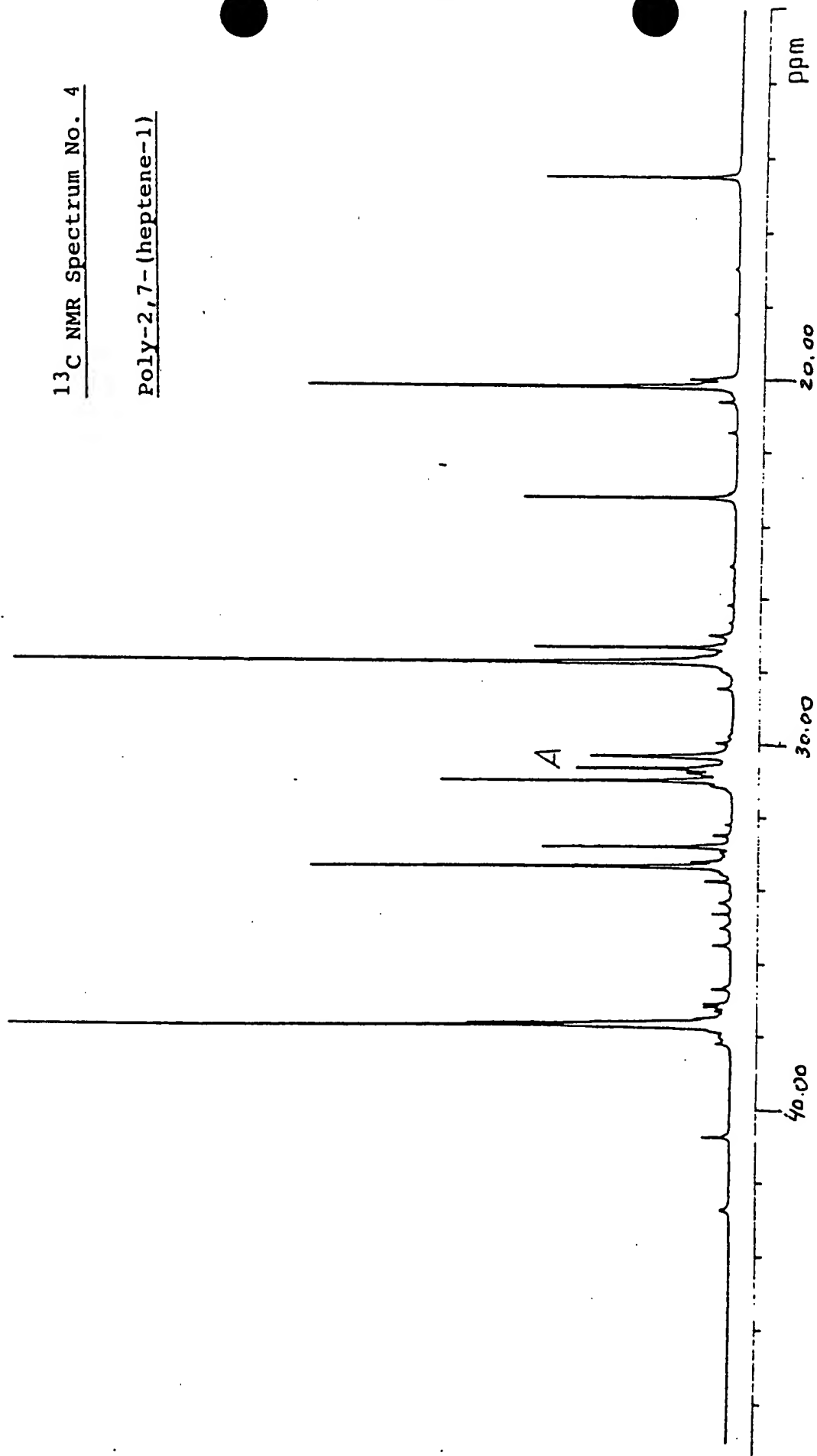
^{13}C NMR Spectrum No. 3

Poly-2,6-(hexene-1)



^{13}C NMR Spectrum No. 4

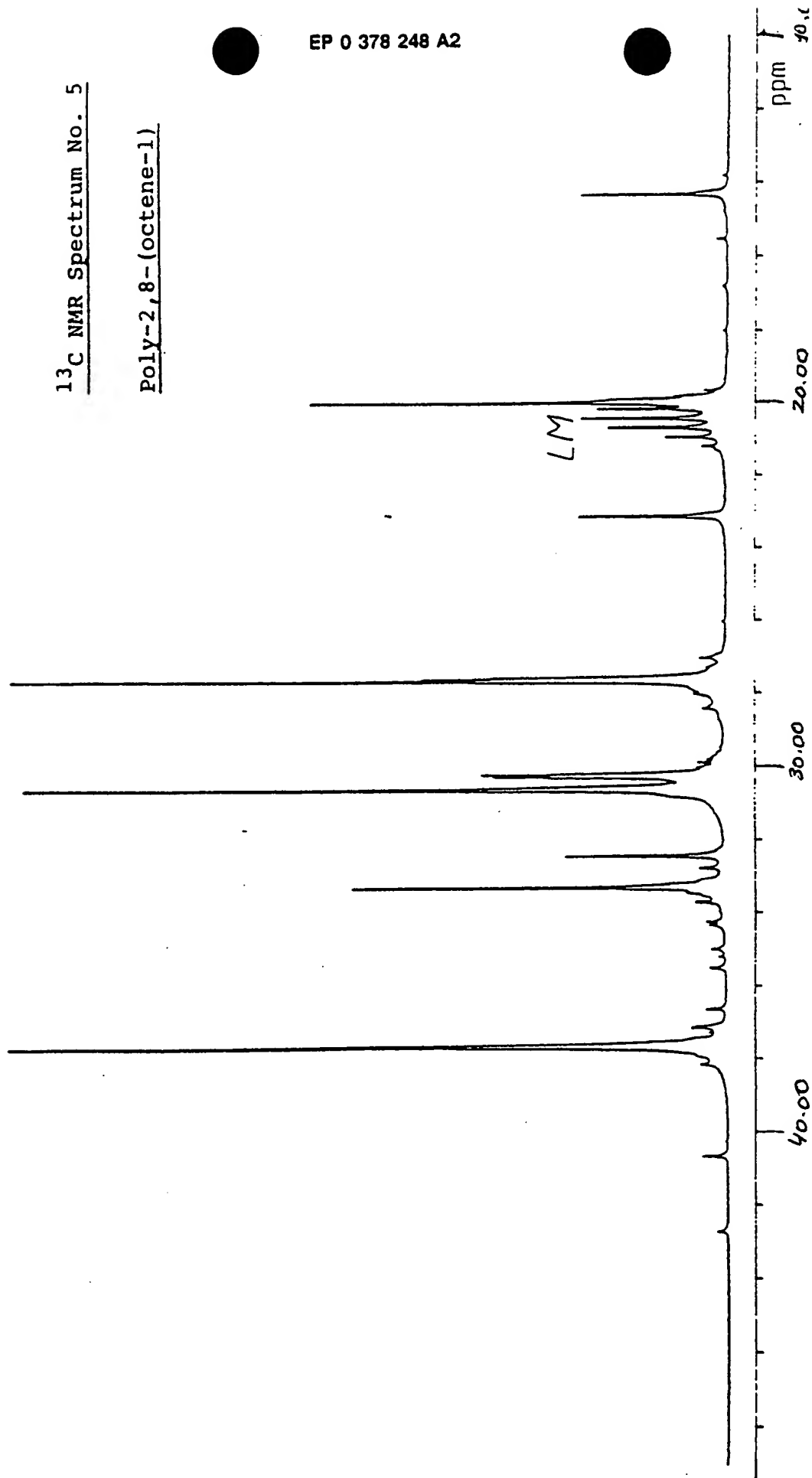
Poly-2,7-(heptene-1)



^{13}C NMR Spectrum No. 5

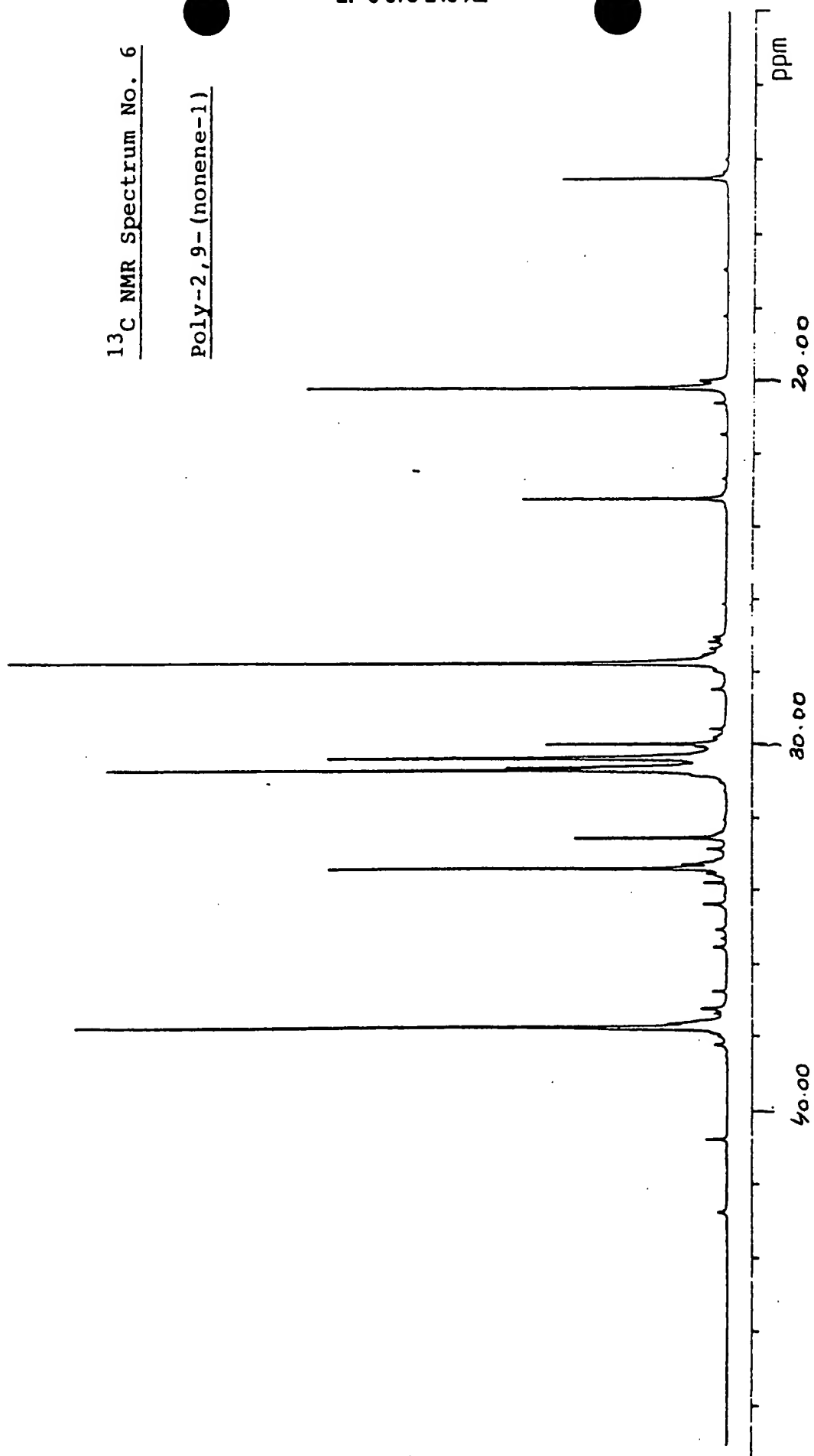
Poly-2,8-(octene-1)

EP 0 378 248 A2



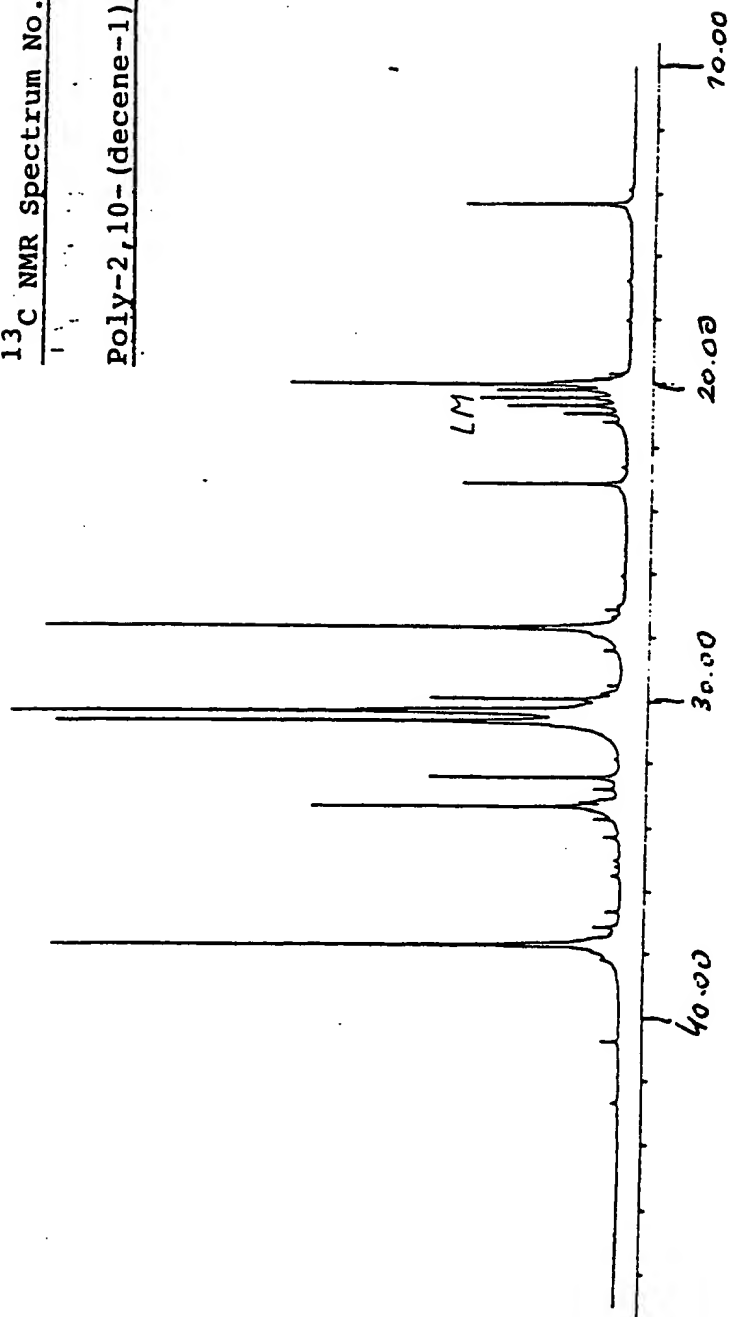
^{13}C NMR Spectrum No. 6

Poly-2,9-(nonene-1)



^{13}C NMR Spectrum No. 7

Poly-2,10-(decene-1)



19



Europäisches Patentamt
European Patent Office
Office européen des brevets

11 Publication number:

**0 378 248
A3**

12

EUROPEAN PATENT APPLICATION

21 Application number: 90103567.5

51 Int. Cl.⁵: **C08F 10/04, C08F 10/14**

22 Date of filing: 12.02.86

30 Priority: 13.02.85 DE 3504809

43 Date of publication of application:
18.07.90 Bulletin 90/29

60 Publication number of the earlier application in
accordance with Art.76 EPC: 0 194 456

64 Designated Contracting States:
AT BE CH DE FR GB IT LI LU NL

66 Date of deferred publication of the search report:
01.08.90 Bulletin 90/31

71 Applicant: Studiengesellschaft Kohle mbH
Kaiser-Wilhelm-Platz 1
D-4330 Mülheim/Ruhr(DE)

72 Inventor: Fink, Gerhard, Dr.
Lembkestrasse 5
D-4330 Mülheim/Ruhr(DE)
Inventor: Möhring, Volker
Lembkestrasse 5
D-4330 Mülheim/Ruhr(DE)

74 Representative: von Kreisler, Alek,
Dipl.-Chem. et al
Patentanwälte Von Kreisler-Selting-Werner
Deichmannhaus am Hauptbahnhof
D-5000 Köln 1(DE)

54 Process for preparing alpha-olefin polymers and oligomers.

57 The invention relates to polymers and oligomers
characterized in that they have been prepared from
 α -olefin monomers or mixtures thereof and the dis-
tances between the methyl branching points are

controllable by the selection of the α -olefins and to a
process for preparing said novel polymers and
oligomers.

EP 0 378 248 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 10 3567

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
	No further relevant documents have been disclosed. -----		C 08 F 10/04 C 08 F 10/14
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 08 F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 10-05-1990	Examiner DE ROECK R.G.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document			